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Tetrazoles as Ligands.
Part IV. Iron(II) Complexes of Monofunctional Tetrazole Ligands, Showing High-Spin ⇋ Low-Spin Transitions

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1-Alkyl substituted tetrazoles and iron(II) tetrafluoroborate lead to the formation of hexacoordinated iron(II) complexes, viz.: $[FeL_6](BF_4)_2$ *with L = 1-methyltetrazole (MTZ), 1-ethyltetrazole (ETZ), 1-propyltetrazole (PTZ) and 1-isopropyltetrazole (IPTZ). The complexes were identified and characterized by elemental analyses, IR and ligand field spectra and magnetic susceptibility measurements. The iron(II) ions are octahedrally surrounded by monodentate ligands and a mononuclear complex formation is obvious. At temperatures varying from 140–80 K the complexes show high-spin* ($^5T_{2g}$) ⇋ *low-spin* ($^1A_{1g}$) *transitions, recognizable by a colour change from white to purple. The transitions were followed by magnetic measurements.*

Introduction

Spin crossover, also referred to as high-spin ⇋ low-spin transition or magnetic crossover, is an extensively studied phenomenon. Based on the valence-bond theory, Pauling proposed long ago the possibility of a spin crossover. By ligand field theory, one can also predict the spin crossover possibility; the Tanabe-Sugano diagram [1] for the d^6 configuration in an octahedral field shows a value for the ligand field strength beyond which the ground state of the iron(II) changes from $^5T_{2g}$ to $^1A_{1g}$. When the field strength around the metal ion lies near this value (the transition region), a relatively small variation in temperature or pressure may change the ground state. The transition can be considered as a chemical reaction with $\Delta G_{HS/LS} = \Delta H - T\Delta S$.

Nevertheless, spin transitions in iron(II) systems were only first described in detail about fifteen years ago. Since then a large number of examples has been reported, surveyed up to 1975 by Goodwin [2]. Except for the iron(II) isoxazole solvate prepared by Driessen and van der Voort [3], all of these examples were found in iron(II) complexes with multidentate ligands. The isoxazole complex was the first example of an iron(II) complex with monodentate ligands and also an example of a system in which the deviation from octahedral symmetry seemed to be very small.

We now report the preparation and characterizations of four new members of this class, iron(II) complexes with monodentate 1-substituted tetrazoles as ligands.

The complexes could be obtained as crystalline solids with crystals of good quality, rather stable towards oxygen and moisture. Structure determinations, Mössbauer effect measurements and low temperature far IR measurements are in progress and will shortly be published. Some initial structural data are already available [4].

In a previous communication [5] we described the preparation and characterization of first row transition metal(II) tetrafluoroborate complexes of MTZ, ETZ and PTZ. Very high Dq-values were found for these monodentate ligands. With regard to the same ligand, the Mn, Co, Ni, Cu and Zn complexes are isomorphous; the same pattern was found for the IR spectra and the X-ray powder diffractograms. The complexes are apparently mononuclear, possess octahedral symmetry, and contain monodentate ligands, coordinating via the N(4) tetrazole atom (Fig. 1).

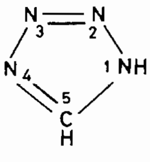

Fig. 1. The tetrazole molecule.

These remarkable properties of the 1-substituted tetrazoles inspired us to prepare more members of this class; 1-isopropyltetrazole, 1-tertiarybutyltetrazole, 1-n-hexyltetrazole and 1-n-dodecyltetrazole. The transition metal(II) complexes were prepared, and we showed that the IPTZ complexes were similar to the MTZ, ETZ and PTZ complexes [6].

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TABLE I. Iron(II) Complexes of 1-Substituted Alkyltetrazoles and their Chemical Analyses.

Complex	Analyses, found (calcd.) (%)			
	M	C	H	N
$[Fe(MTZ)_6](BF_4)_2$	7.4(7.6)	19.6(19.6)	3.8(3.3)	45.9(45.8)
$[Fe(ETZ)_6](BF_4)_2$	6.6(6.8)	26.0(26.4)	4.5(4.4)	40.4(41.1)
$[Fe(PTZ)_6](BF_4)_2$	6.1(6.2)	31.8(31.7)	5.4(5.9)	37.4(37.0)
$[Fe(IPTZ)_6](BF_4)_2$	6.0(6.2)	31.8(31.7)	5.4(5.9)	37.3(37.0)

TABLE II. Some Characteristic IR Absorption Bands of the 1-Alkyltetrazoles and their Complexes.

Assignment	MTz	Fe(MTz)	ETz	Fe(ETz)	PTz	Fe(PTz)	IPTz	Fe(IPTz)
$\nu(CH_r)$[a]	3138s	3157s	3138s	3152s	3138s	3144s	3130m	3138s
$\nu(CH_a)$	2962m	2961m	2991s	2999s	2985s	2987m	2982s	2982m
$\nu(CH_a)$	2930w	2928w	2950m	2951m	2940m	2941m	2940m	2943w
(CH_a)	–	–	2890w	2888w	2882m	2888w	2850w	–
ρ[b]	1499vs	1518s	1490vs	1512s	1490s	1509s	1472s	1493s
ρ	1278s	1279m	1260vs	1288m	1271m	1281m	1275m	1300m
ρ	1175vs	1190s	1175vs	1182s	1173vs	1180s	1183vs	1186s
ρ	1111vs	1114s	1115vs	1098m	1111vs	1100m	1101s	1099vs
ρ[c]	1049m	–	1052m	–	1048m	–	1062w	–
ρ[c]	1017m	–	1026m	–	1021m	–	1022m	–
ρ	967s	992s	974vs	996s	966s	997s	972m	992s
o.o.p.CH_a	–	–	801s	800m	805s	805s	940s	940w
o.o.p.CH_r	881s	900s	877s	896m	879s	898s	890s	899m
τ	681vs	688vs	681vs	681vs	680vs	673s	681vs	679s
τ	650vs	659vs	650vs	650vs	659vs	646s	635s	635s

[a] CH_r = ring CH; CH_a = alkyl CH. [b] ρ = i.p. ring vibration, τ = O.O.P. ringvibration. [c] These bands are obscured by BF_4^- absorptions in the complexes.

Experimental

$[Fe(H_2O)_6](BF_4)_2$ was prepared from Fe and an aqueous HBF_4 solution (35%) and was recrystallized from H_2O.

The alkyltetrazoles were prepared from the alkylaminehydrochlorides, NaN_3 and $HC(OEt)_3$ in HOAc [7], purified by neutralization with $NaHCO_3$ and extraction with $CHCl_3$. After drying the $CHCl_3$ layer, the solvent was distilled off and the remaining liquid was distilled under reduced pressure to give the tetrazoles.

The complexes were prepared by the following method.

Preparation method

The Fe(II) tetrafluoroborate hexahydrate (2 mmol) was dissolved in 10 ml H_2O. To this solution the alkyltetrazole (13 mmol), dissolved in a few ml EtOH, was added. The solution was stirred and slightly heated (40 °C) until a clear and homogeneous solution was obtained; undissolved material was removed by means of quick filtration through a glass filter. The complexes crystallized slowly on standing in air, when fine, colourless leaves were obtained. The crystals were collected on a glass filter washed with a cold $CHCl_3$/acetone mixture and air-dried.

Carbon, hydrogen and nitrogen elemental analyses were carried out in the laboratory of Dr. Pascher [8] and the metal contents were determined complexometrically after prior decomposition with HNO_3. Details are given in Table I.

IR measurements were carried out on a Perkin-Elmer 580 spectrophotometer in the 4000–180 cm^{-1} region. The samples were measured as the pure liquids (for ETZ, PTZ and IPTZ), as emulsions in nujol between KRS5 windows and as pellets with KBr. For the far IR region (500–180 cm^{-1}) nujol mulls between polyethene windows were used. For the low temperature measurements the sample holder was cooled with liquid nitrogen.

Ligand field spectra were recorded on a Beckman DK2A UV-Vis. spectrophotometer in the 2000–350 nm region.

Magnetic susceptibility measurements were carried out on a Mettler Faraday balance from 77-300 K.

Tables II and III give IR and far IR data, Table IV gives magnetic data.

TABLE III. Far IR Absorption Bands of the Iron(II) 1-Alkyltetrazole Complexes and a Description of the Absorptions.

$[Fe(MTZ)_6](BF_4)_2$	$[Fe(ETZ)_6](BF_4)_2$	$[Fe(PTZ)_6](BF_4)_2$		$[Fe(IPTZ)_6](BF_4)_2$	Descr.
		296 K	90 K		
523 s	523 s	523 s	525 s	524 s	νBF_4^-
479 w	488 w	474 m	–	493 m	δ (NC)
–	425 m	–		425 w	Alkyl
–	–	–	415 m	–	ν(M–N)LS
–	–	–	398 w	–	?
377 m	–	375 m	–	–	γ(NC)
361 m	365 m	–	360 m	365 w	γ(NC)
–	–	–	309 w	–	?
270 sh	290 sh	286 s	292 s	270 m	?
–	–	–	265 m	–	?
226 vs	228 vs	227 vs	236 m	217 vs	ν(M–N)HS

TABLE IV. Magnetic Data for the Iron(II) 1-Alkyltetrazole Complexes.

	MTZ	ETZ	PTZ	IPTZ
$\mu_{eff.}$(BM) 300 K	5.2	4.85	5.75	5.75
$\mu_{eff.}$(BM) 77 K	2.3	3.3	0.65	4.64
Transition region (K)	120–80	–	140–100	–

Results and Discussion

The iron(II) complexes are crystalline colourless solids; the crystals are of good quality, stable towards oxidation by air oxygen, and are not hygroscopic. When cooled in liquid nitrogen, the colour of the compounds changes into deep purple, indicating a spin-crossover that changes the groundstate from $^5T_{2g}$ to $^1A_{1g}$.

Initial structural indications are gained from the stoïchiometry of the compounds. A mononuclear complex formation with monodentate ligands is obvious. The symmetry of the chromophore is probably octahedral.

Evidence for these assumptions was obtained from IR spectra and X-ray powder diffractograms. The iron(II) complexes appeared to be isomorphous with the transition metal(II) complexes with the same ligand [5]. Therefore we assume that the iron(II) complexes have regular octahedral symmetry, the coordination site of the tetrazole being probably the N(4) atom. More support was obtained from single crystal X-ray diffraction measurements on $[Fe(ETZ)_6](BF_4)_2$ and $[Fe(PTZ)_6](BF_4)_2$ [4], Mössbauer measurements [9] and ligand field spectral data (*vide supra*). From the X-ray diffraction data indications were obtained of a very regular octahedron with Fe–N distances of 2.15 Å. The coordination site of the ring appeared to be the N(4) atom as assumed before.

IR spectra were recorded for identification and show the presence of coordinated 1-alkyltetrazoles. As expected, the tetrafluoroborate anions do not take part in the coordination. In Table II some characteristic absorption bands of the ligands and complexes are collected. The assignment, based on data from previous papers [5, 10], is limited to the tetrazole ring vibrations and some C–H vibrations.

Far IR measurements were carried out to obtain more information about the nature and the strength of the metal-to-ligand (M–L) bond in the high-spin state. Low temperature measurements were carried out to investigate the possibilities of a low temperature far IR study to obtain information about the low-spin state. Acceptable results were obtained for the PTZ complex.

As can be seen from Table III, the absorptions are found in the usual region for strong nitrogen-donating ligands. The absorptions are found at values ranging between the absorption values of the Mn–L and Co–L stretching vibrations [5], and therefore fit in the Irving-Williams sequence, providing some evidence for the assignment in Table III. The remaining bands are absorptions of the ligands and anions (see description).

The low temperature measurements gave comparable results for the PTZ complex. The most important changes in the far IR part of the spectrum are the increase and decrease of several bands; while decreasing, the bands also shift to higher values. The band, assigned to ν(M–N) looses intensity with decreasing temperature and is only weak present at 90 K. The band also shifts from 227 to 236 cm^{-1}. New bands appear at 90 K; at 415, 398, 360, 309 and 265

cm^{-1}. The bands at 415 and 360 cm^{-1} are more intensive than the other new bands and one of these two is probably the ν(M–N) in the low spin state. Figure 2 gives the room and low temperature spectrum of the $[Fe(PTZ)_6](BF_4)_2$ complex and a tentative assignment is given in Table III.

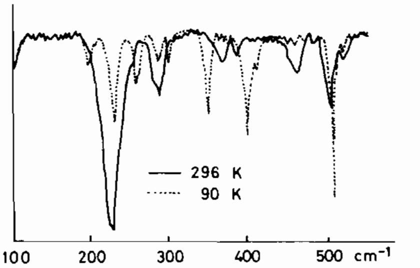

Fig. 2. Far IR spectra of $[Fe(PTZ)_6](BF_4)_2$ at 296 and 90 K.

Shifts of about 200 cm^{-1} are not rare for the ν(M–N) in HS and LS states. For $[Fephen_2X_2]$, $[Febipy_2X_2]$ [11–15] and $[Fe(pic)_3]Cl_2$ EtOH [16] shifts of the same magnitude were found. The shift to higher energies implies M–N bond strengthening, consistent with the bond-shortening revealed by structure determinations [17–19].

Ligand field spectra of the complexes show only one sharp band, from 11500–11900 cm^{-1}, due to the absorption of the $^5E_{1g} \leftarrow {}^5T_{2g}$ transition, supplying more evidence for regular O_h-symmetry. For distorted octahedrons (D_{4h}-symmetry) higher values for the transition are expected, because in tetragonally distorted Fe(II) compounds the $^5T_{2g}$ level splits into a $^5E_{2g}$ state of lower energy and a $^5B_{2g}$ state of higher energy and the $^5E_{1g}$ level into a $^5A_{1g}$ of lower and a $^5B_{1g}$ state of higher energy. Figure 3 gives a schematic picture of these splittings. The expected ligand field transitions now are $^5A_{1g} \leftarrow {}^5E_{2g}$ and $^5B_{1g} \leftarrow {}^5E_{2g}$. These two transitions appear in most cases as one broad and at higher values than the transitions in the O_h case. Because the transitions in our case appear in the spectrum as one sharp band at relatively low values we assume that the symmetry about the Fe(II) ion does not deviate much from O_h.

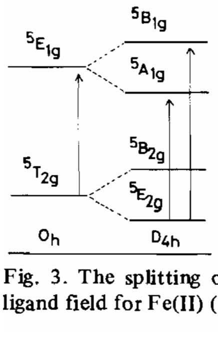

Fig. 3. The splitting of the octahedral terms in a tetragonal ligand field for Fe(II) (schematically).

The possibility to predict a HS ⇋ LS transition in an iron(II) complex from the Dq value of the corresponding Ni(II) complex has been suggested by several investigators [20, 21]. The values of the ligand field transitions of our Fe compounds correspond very well with the Dq values of the Ni(II) complexes [5]. These Ni(II) Dq values fit very well in the range established by Robinson *et al.* [20]. The range suggested by Nelson and Rodgers [21] however seems to be incorrect with regard to our compounds.

Magnetic susceptibility measurements from 300–77 K were carried out to obtain information about the transition temperature and the value of the magnetic moment in both states. Although the complexes show similarities with regard to their structures, the magnetic behaviour of the compounds is different.

The value of the effective magnetic moment in the high-spin state should be approximately 5.3 BM and in the low-spin state about 0.5 BM.

A thermally induced $^1A_{1g} \rightleftharpoons {}^5T_{2g}$ transition should result in a strong temperature dependence of the moment, and a variation from about 5.3 to 0.5 might be expected. Figure 4 shows the temperature dependence of the complexes, the PTZ complex shows the expected picture: in a rather narrow temperature range (about 130 K) the moment drops from 5.75 to 0.64 BM and is virtually complete.

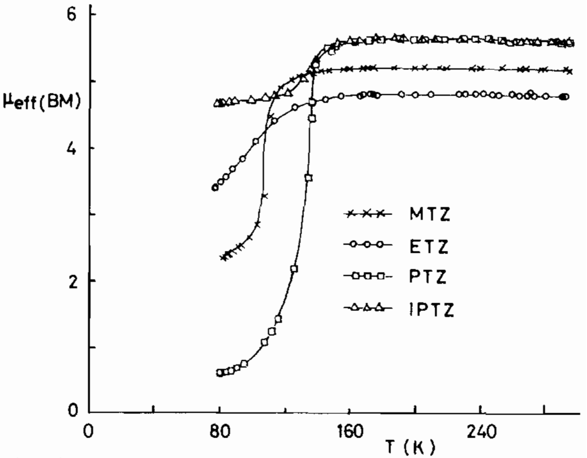

Fig. 4. Plots of the effective magnetic moment *vs.* the temperature.

The transition in the MTZ complex shows an identical pattern but seems to be incomplete. It is possible that the moment will drop further at lower temperatures. It is also possible that a time effect occurs and the moment drops after a long period of cooling. These possibilities are being investigated.

The ETZ and IPTZ complexes still have large moments at 77 K and it is likely to assume that impurities of Fe(III) or large residual $^5T_{2g}$ fractions cause these high moments.

In short time we hope to come to more conclusive results with the help of Mössbauer and 4 K magnetic Phoner measurements.

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